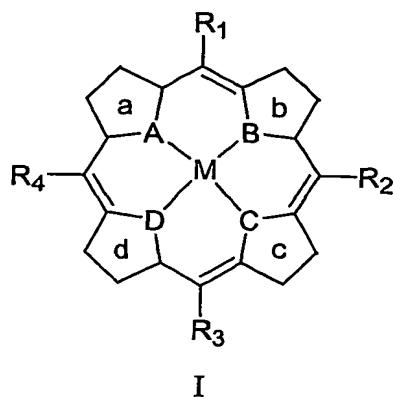


76  
CLAIMS

1. A compound of formula I, or a pharmaceutically acceptable salt thereof,



wherein

one or two of A, B, C and D are each independently selected from S, O, Se and Te, and the remainder are N;

a, b, c and d are each independently substituted or unsubstituted 5-membered heterocyclic groups having the members necessary to complete a porphyrin, chlorin, bacteriochlorin or isobacteriochlorin nucleus in which one or two of the nitrogens are replaced by S, O, Se or Te;

M is H or a metal;

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each independently selected from:

H;

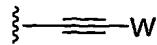
alkyl;

cycloalkyl;

halogen;

aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, COOH, COO-alkyl, -OZ, -COOZ, a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative,

$-C\equiv C-(CH_2)_pCO_2R_{10}$ , where  $R_{10}$  is H or alkyl, and  $O(CH_2)_rCOR_{11}$ , where  $R_{11}$  is OH, O-alkyl or N-succinimide, and p and r are each independently an integer from 1 to 10;



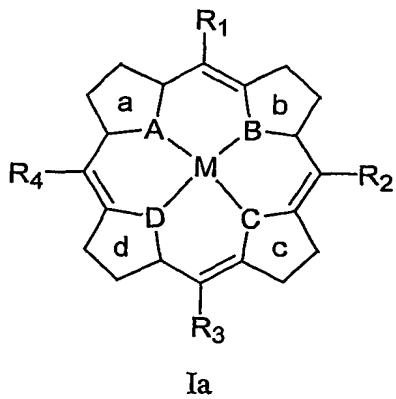
wherein W is an aryl, alkyl or heteroaryl group, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $CF_3$ , alkyl, alkoxy, halogen, an isothiocyanate group, a haloacetamide, maleimide,  $NH_2$ ,  $NO_2$ ,  $CONH_2$ , haloalkyl, COOH,  $COO$ -alkyl,  $-OZ'$ ,  $-COOZ'$ , a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative,  $-C\equiv C-(CH_2)_pCO_2R_{12}$ , where  $R_{12}$  is H or alkyl, and  $O(CH_2)_rCOR_{13}$ , where  $R_{13}$  is OH, O-alkyl or N-succinimide, and p' and r' are each independently an integer from 1 to 10;

where Z and Z' are each independently silicon-containing protecting groups;

and wherein when a, b, c and d have the members necessary to complete a porphyrin nucleus in which one or two of the nitrogens are replaced by S, O, Se or Te,

- (a)  $R_1, R_2$  and  $R_3$  are identical, and  $R_4 \neq R_1, R_2, R_3$ ; or
- (b)  $R_1 = R_3$ ;  $R_2 = R_4$ , where  $R_1, R_3 \neq R_2, R_4$ ; or
- (c)  $R_2 = R_3$ ;  $R_1 \neq R_4$ ; and  $R_1, R_4 \neq R_2, R_3$ .

2. A compound of formula Ia



wherein

one or two of A, B, C and D are each independently selected from S, O, Se and Te, and the remainder are N;

a, b, c and d are each independently substituted or unsubstituted 5-membered heterocyclic groups having the members necessary to complete a chlorin, bacteriochlorin or isobacteriochlorin nucleus in which one or two of the nitrogens are replaced by S, O, Se or Te;

M is H or a metal;

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each independently selected from:

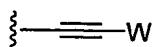
H;

alkyl;

cycloalkyl;

halogen;

aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, haloalkyl, COOH, COO-alkyl, -OZ, -COOZ, a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative, -C≡C-(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>R<sub>10</sub>, where R<sub>10</sub> is H or alkyl, and O(CH<sub>2</sub>)<sub>r</sub>COR<sub>11</sub>, where R<sub>11</sub> is OH, O-alkyl or N-succinimide, and p and r are each independently an integer from 1 to 10;



wherein W is an aryl, alkyl or heteroaryl group, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, haloalkyl, COOH, COO-alkyl, OZ', COOZ', a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative, -C≡C-(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>R<sub>12</sub>, where R<sub>12</sub> is

H or alkyl, and  $O(CH_2)_rCOR_{13}$ , where  $R_{13}$  is OH, O-alkyl or N-succinimide, and  $p'$  and  $r'$  are each independently an integer from 1 to 10;  
where  $Z$  and  $Z'$  are each independently silicon-containing protecting groups.

3. A compound according to claim 1 or claim 2 wherein one of A, B, C and D is S and the remainder are all N.

4. A compound according to any preceding claim wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each independently selected from:

H;

halogen;

phenyl or pyridyl, each of which are optionally substituted by one or more substituents selected from OH, CN,  $CF_3$ , alkyl, alkoxy, haloalkyl, halogen,  $NH_2$ ,  $NO_2$ ,  $CONH_2$ , haloalkyl, COOH, COO-alkyl, OZ,  $COOZ$ , a polyethylene glycol group,  $-C\equiv C-(CH_2)_pCO_2R_{10}$ , where  $R_{10}$  is H or alkyl, and  $O(CH_2)_rCOR_{11}$ , where  $R_{11}$  is OH, O-alkyl or N-succinimide, and  $p$  and  $r$  are each independently an integer from 1 to 10;



wherein W is a phenyl or pyridyl group, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $CF_3$ , alkyl, alkoxy, haloalkyl, halogen,  $NH_2$ ,  $NO_2$ ,  $CONH_2$ , haloalkyl, COOH, COO-alkyl, OZ',  $COOZ'$ , a polyethylene glycol group,  $-C\equiv C-(CH_2)_pCO_2R_{12}$ , where  $R_{12}$  is H or alkyl, and  $O(CH_2)_rCOR_{13}$ , where  $R_{13}$  is OH, O-alkyl or N-succinimide, and  $p'$  and  $r'$  are each independently an integer from 1 to 10.

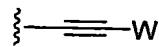
5. A compound according to any preceding claim wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each independently selected from:

H;

halogen;

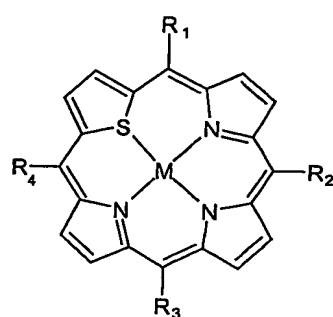
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phenyl or pyridyl, each of which are optionally substituted by one or more substituents selected from alkoxy, halogen, OH,  $O(CH_2)_rCOR_{11}$  and  $-C\equiv C-(CH_2)_pCO_2R_{10}$ ;



wherein W is phenyl or pyridyl, each of which may be optionally substituted by one or more substituents selected from OH, OZ' and a polyethylene glycol group.

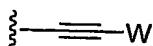
6. A compound according to any one of claims 1, 3, 4 or 5 which is of formula II



III

7. A compound according to claim 6 wherein

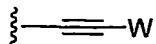
$R_1$  and  $R_4$  are different and are selected from aryl and heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $CF_3$ , alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide,  $NH_2$ ,  $NO_2$ ,  $CONH_2$ , haloalkyl, COOH, COO-alkyl, OZ and COOZ; and  $R_2$  and  $R_3$  are the same and are both H, halogen or



8. A compound according to claim 7 wherein

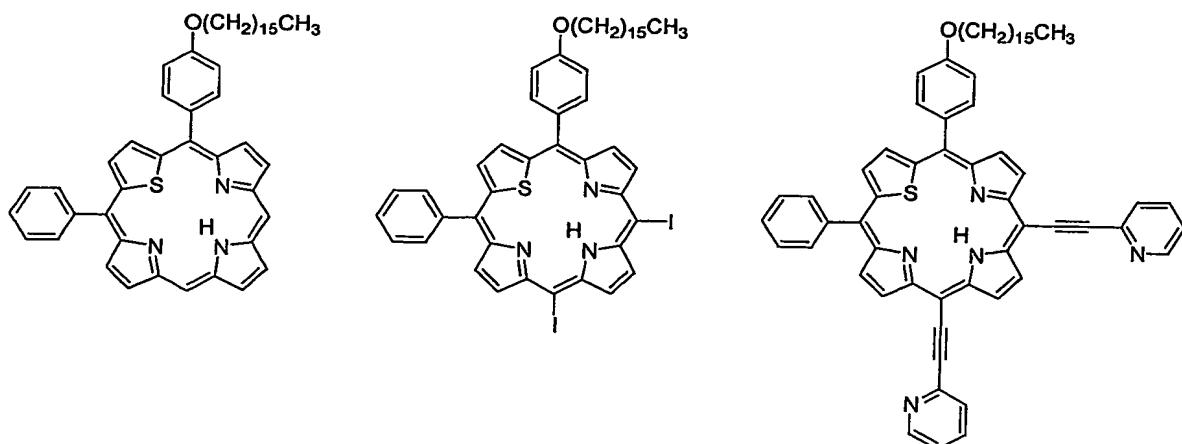
$R_1$  is aryl optionally substituted by an alkoxy group:

$R_2$  and  $R_3$  are both H, halogen or

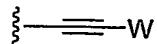


where W is a pyridyl;  
R<sub>4</sub> is phenyl.

9. A compound according to claim 8 which is selected from the following:

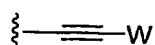


10. A compound according to claim 6 wherein  
R<sub>1</sub> are R<sub>3</sub> are the same and are both H, halogen or



R<sub>2</sub> and R<sub>4</sub> are the same and are both aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, haloalkyl, COOH, COO-alkyl, OZ and COOZ.

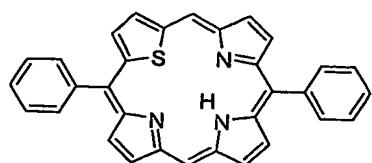
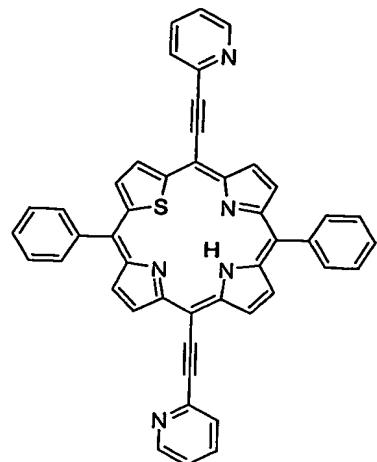
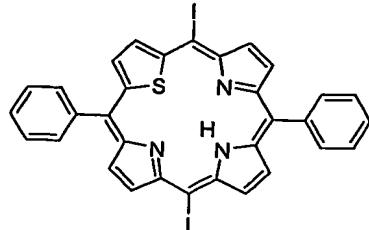
11. A compound according to claim 10 wherein  
R<sub>1</sub> and R<sub>3</sub> are both H, halogen or



where W is pyridyl;  
R<sub>2</sub> and R<sub>4</sub> are both phenyl.

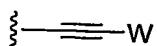
82

12. A compound according to claim 11 which is selected from the following:



13. A compound according to claim 6 wherein

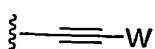
$R_1$ ,  $R_2$  and  $R_3$  are the same and are all H, halogen or



$R_4$  is aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $CF_3$ , alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide,  $NH_2$ ,  $NO_2$ ,  $CONH_2$ , haloalkyl, COOH,  $COO$ -alkyl, OZ,  $COOZ$ ,  $-C\equiv C-(CH_2)_pCO_2R_{10}$ , where  $R_{10}$  is H or alkyl, and  $O(CH_2)_rCOR_{11}$ , where  $R_{11}$  is OH, O-alkyl or -N-succinimide, and p and r are each independently an integer from 1 to 10.

14. A compound according to claim 13 wherein

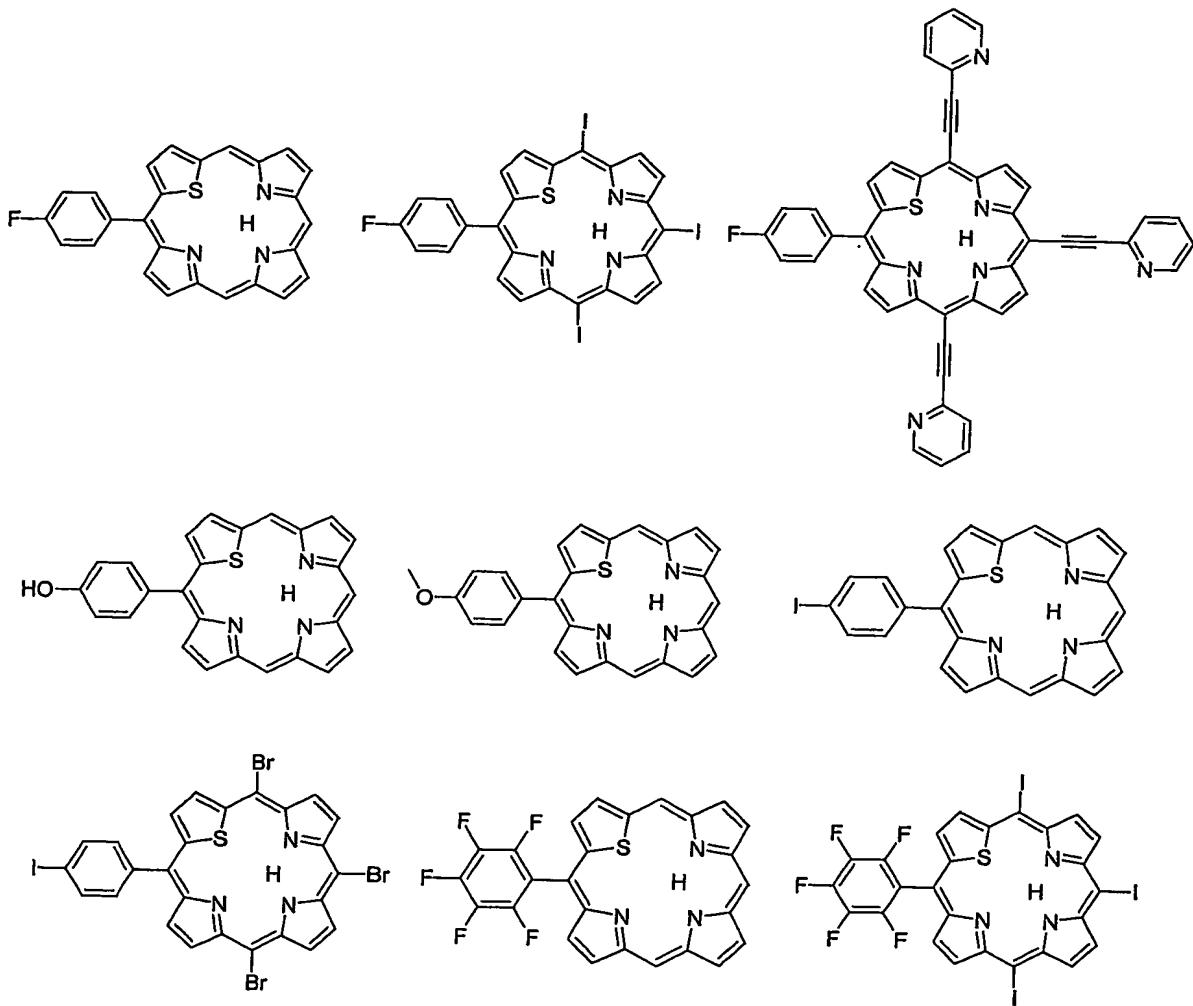
$R_1$ ,  $R_2$  and  $R_3$  are all H, halogen or



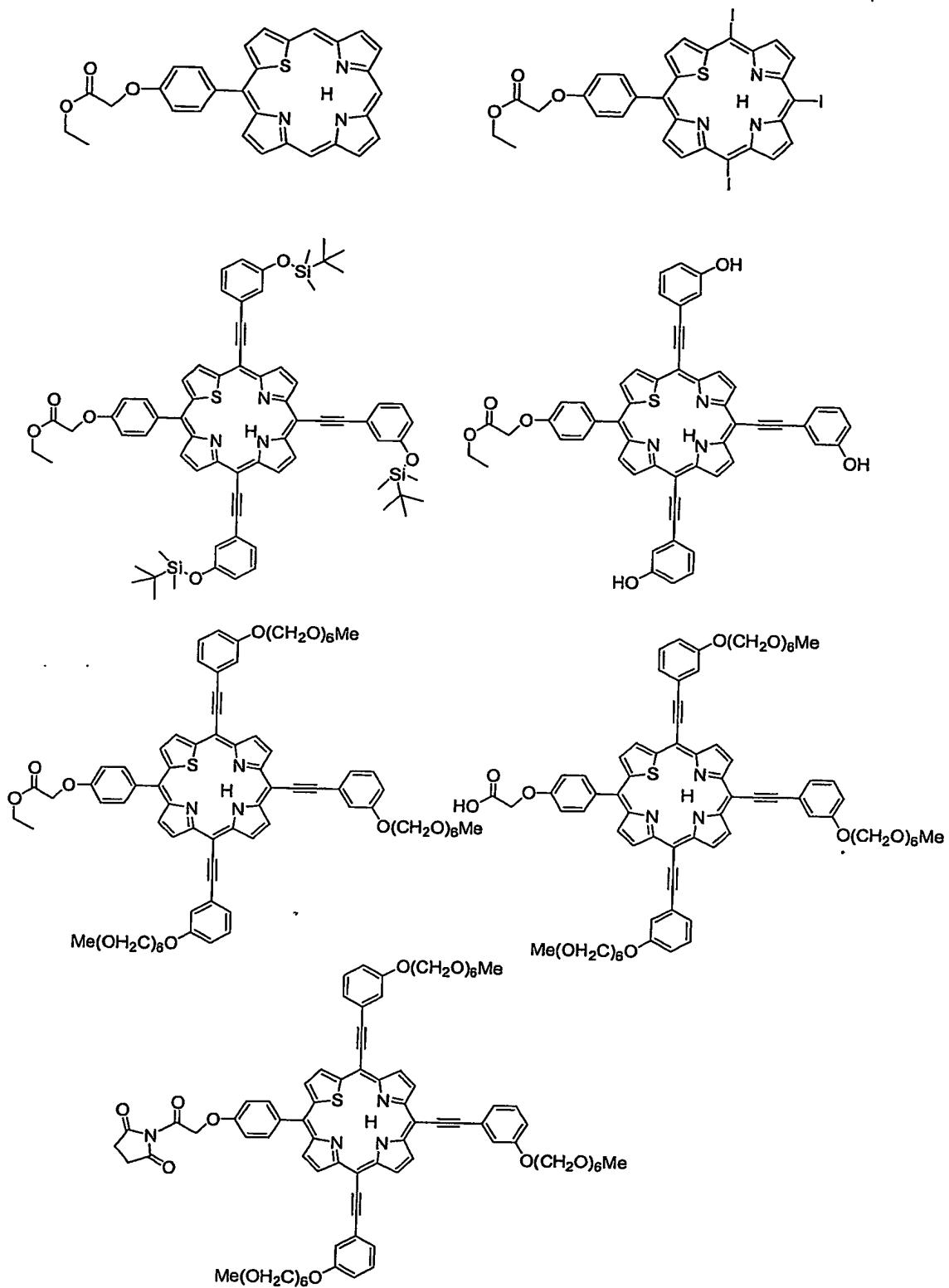
where W is a pyridyl or phenyl group, each of which may be optionally substituted by one or more substituents selected from OH, OZ', and a polyethylene glycol group; and  $R_4$  is a phenyl group substituted by one or more halogen, alkoxy,  $O(CH_2)_pCOR_{11}$  or  $-C\equiv C-(CH_2)_pCO_2R_{10}$  groups.

83

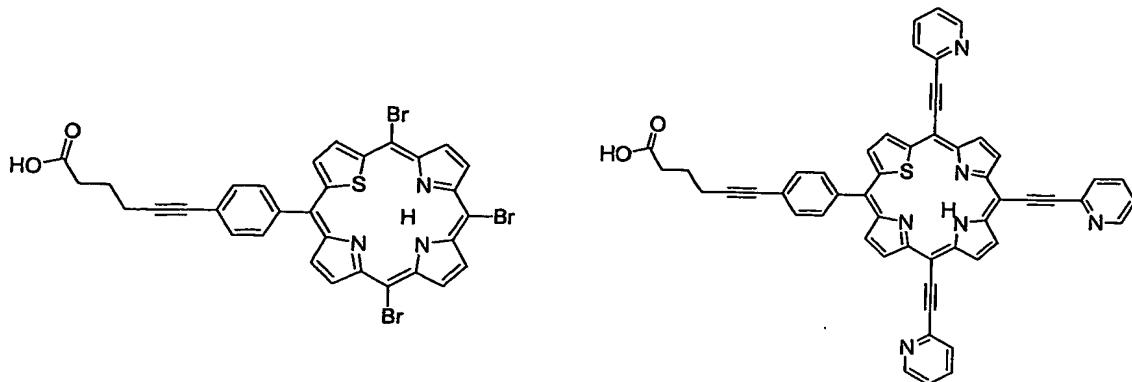
15. A compound according to claim 14 wherein said compound is selected from the following:



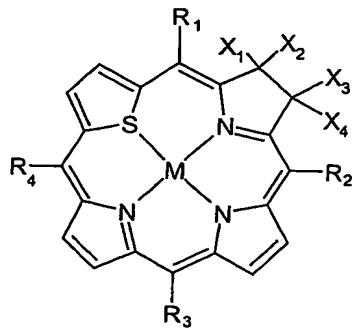
84



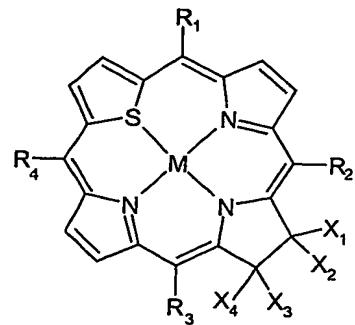
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16. A compound according to any one of claims 1 to 5 which is of formula III or IV



III

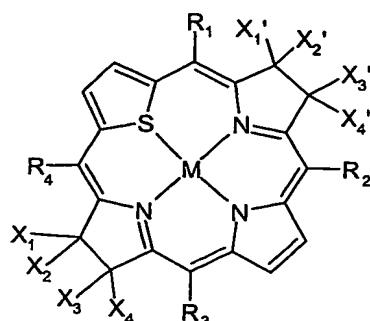


IV

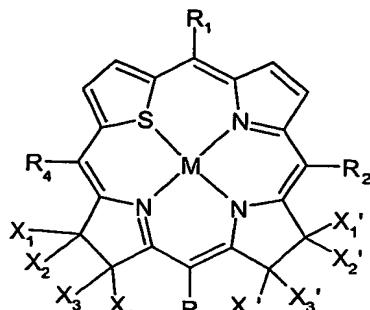
wherein X<sub>1</sub>-X<sub>4</sub> are each independently selected from H, OH, alkyl, alkoxy; or C=O, where X<sub>2</sub> and X<sub>4</sub> respectively are absent, and R<sub>1</sub>-R<sub>4</sub> and M are as defined in claim 1.

17. A compound according to claim 16 wherein X<sub>1</sub> and X<sub>3</sub> are OH, and X<sub>2</sub> and X<sub>4</sub> are H.

18. A compound according to any one of claims 1 to 5 which is of formula V or VI



V

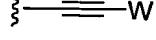


VI

wherein R<sub>1</sub>-R<sub>4</sub> and M are as defined in claim 1, and X<sub>1</sub>-X<sub>4</sub> and X<sub>1'</sub>-X<sub>4'</sub> are each independently selected from H, OH, alkyl, alkoxy; or C=O, where X<sub>2</sub>, X<sub>4</sub>, X<sub>2'</sub> and X<sub>4'</sub> respectively are absent.

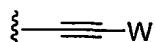
19. A compound according to claim 18 wherein X<sub>1</sub>, X<sub>3</sub>, X<sub>1'</sub> and X<sub>3'</sub> are OH, and X<sub>2</sub>, X<sub>4</sub>, X<sub>2'</sub> and X<sub>4'</sub> are all H.

20. A compound according to claim 16 or claim 18 wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are the same and are all H, halogen or



R<sub>4</sub> is aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, haloalkyl, COOH, COO-alkyl, OZ and COOZ.

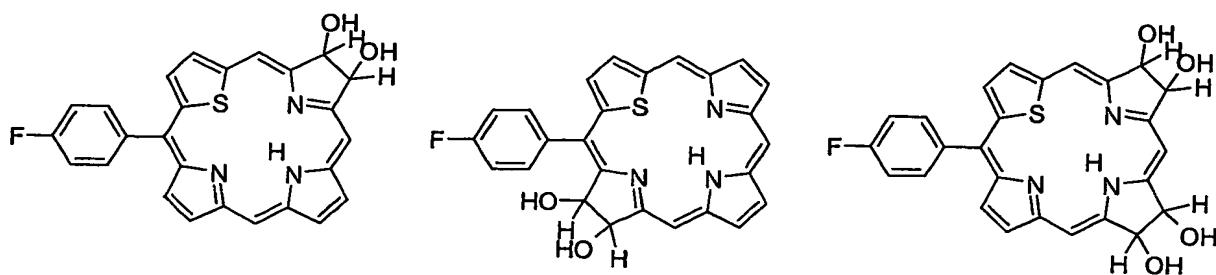
21. A compound according to claim 20 wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are all H, halogen or



where W is pyridyl; and

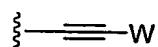
R<sub>4</sub> is a halogen substituted aryl group.

22. A compound according to claim 21 which is selected from:



23. A compound according to claim 16 or claim 18 wherein

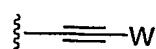
R<sub>2</sub> and R<sub>3</sub> are the same and are both H, halogen or



R<sub>1</sub> and R<sub>4</sub> are different and are aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, haloalkyl, COOH, COO-alkyl, OZ and COOZ.

24. A compound according to claim 23 wherein

R<sub>2</sub> and R<sub>3</sub> are both H, halogen or

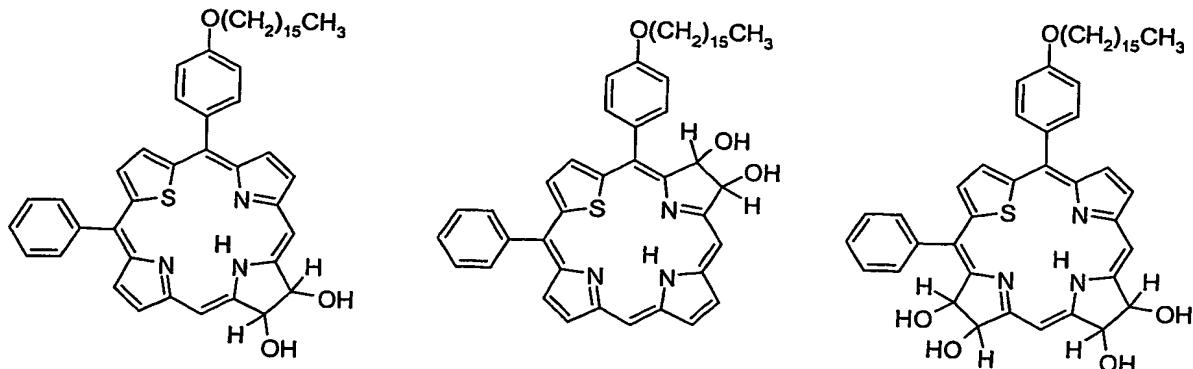


where W is pyridyl;

R<sub>4</sub> is phenyl; and

R<sub>1</sub> is alkoxy substituted phenyl.

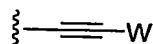
25. A compound according to claim 24 which is selected from:



26. A compound according to claim 16 or claim 18 wherein

$R_1$  and  $R_3$  are the same and are both aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $CF_3$ , alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide,  $NH_2$ ,  $NO_2$ ,  $CONH_2$ , haloalkyl, COOH, COO-alkyl, OZ and COOZ; and

$R_2$  and  $R_4$  are the same and are both H, halogen or

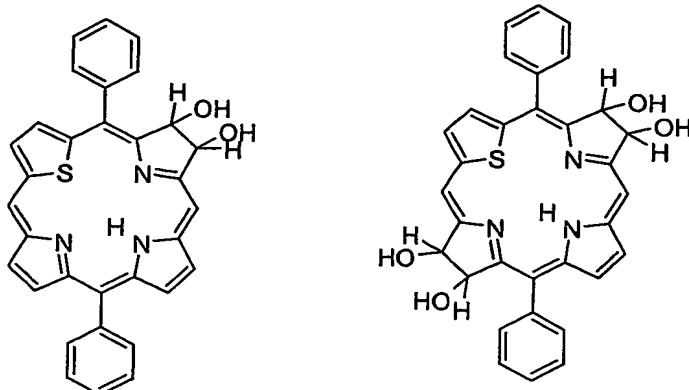


27. A compound according to claim 26 wherein

$R_1$  and  $R_3$  are both phenyl; and

$R_2$  and  $R_4$  are both H.

28. A compound according to claim 27 which is selected from the following:



29. A compound according to any preceding claim wherein M is selected from H, Ni, Pb, V, Pd, Co, Nb, Al, Sn, Zn, Cu, Mg, Ca, In, Ga, Fe, Eu, Lu, Pt, Ru, Mn and Ge.

30. A compound according to any preceding claim wherein M is H or Zn.

31. A pharmaceutical composition comprising a compound according to any one of claims 1 to 30 admixed with a pharmaceutically acceptable diluent, excipient or carrier.

32. A conjugate molecule comprising a compound as defined in any one of claims 1 to 30 and a targeting moiety selected from a recombinant antibody, a Fab fragment, a F(ab')<sub>2</sub> fragment, a single chain Fv, a diabody, a disulfide linked Fv, a single antibody domain and a CDR.

33. A conjugate molecule which comprises a polypeptide carrier comprising at least one alpha helix having synthetically attached thereto a plurality of compounds as defined in any one of claims 1 to 30.

34. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33 in medicine.

90

35. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33, for medical imaging.

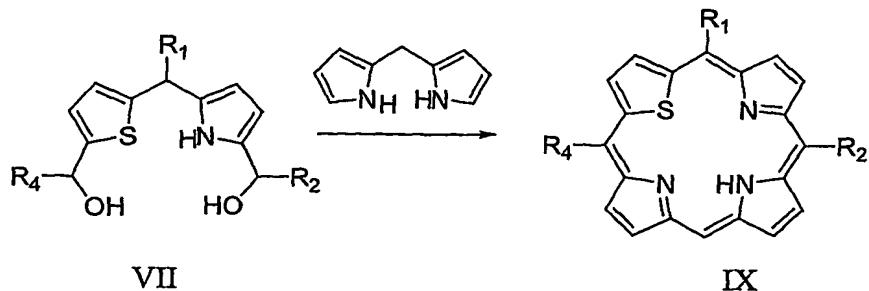
36. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33, in the preparation of a medicament for photodynamic therapy.

37. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33, in the preparation of a medicament for treating a proliferative disorder.

38. Use of a compound according to any one of claims 1 to 30 in the preparation of a conjugate according to claim 32 or claim 33.

39. A method of treating a proliferative disorder, said method comprising administering to a subject a therapeutic amount of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33.

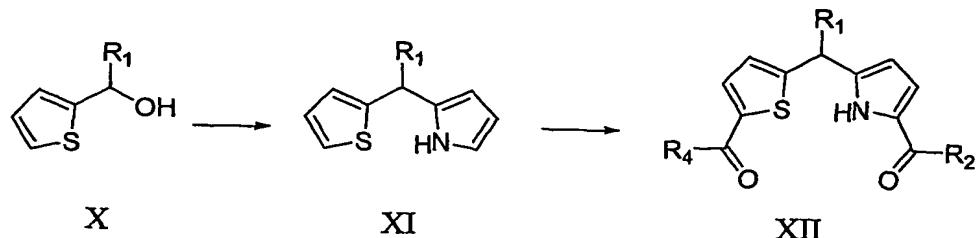
40. A process for preparing a compound as defined in claim 1 or claim 2, said process comprising reacting a compound of formula VII with a dipyrrole to form a compound of formula IX



where R<sub>1</sub>, R<sub>2</sub> and R<sub>4</sub> are as defined in claim 1.

91

41. A process according to claim 40 wherein said compound of formula VII is prepared via intermediates X, XI and XII



42. A process according to claim 40 or claim 41 for preparing a compound according to claim 17 or claim 19 which further comprises oxidising said compound of formula IX with osmium tetroxide.